ENAMELS

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PROTECTIVE HEAT-RESISTANT LEAD-FREE ENAMELS FOR COPPER

E. A. Yatsenko,[1] A. P. Zubekhin,[1] and A. A. Nepomnyashchev[1]

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Based on the $R_2O - CaO - BaO - B_2O_3 - Al_2O_3 - SiO_2$ system, the areas of glass formation are defined and the composition used as a glass matrix for heat-resistant enamels is determined. The effect of Fe_3O_4, Co_2O_3, and MnO_2 additives on adhesion strength and heat stability is investigated. The optimal compositions are identified. The dependence of the structure and phase composition of enamel coatings on the content of the specified additives is established.

An important way to increase the resources of household gas equipment is the development of various methods for protection of copper heat exchangers from scaling and burning-through. The most efficient and technologically adequate protection method is the application of low-melting glass enamel coatings with increased heat resistance, above all, the one-coat enamels.

Since the enamels for copper known from the published sources [1] are mostly lead-silicate with an increased content of lead oxide (up to 60 wt.%), and the protective coatings for heat-exchangers, besides increased heat resistance and high adhesion strength, have to meet environmental requirements, another extremely important problem involves the synthesis of lead-free protective enamels.

[1] Novocherkassk State Technical University, Novocherkassk, Russia.

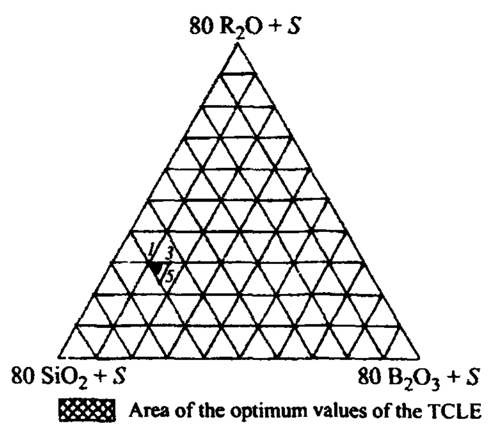

Fig. 1. Area of low-melting glass in the R_2O (Na_2O, K_2O) – CaO – BaO – B_2O_3 – Al_2O_3 – SiO_2 system. S = $7Al_2O_3 + 5CaO + 8BaO$.

Based on preliminary studies carried out at the Novocherkassk State Technical University, the following mass content of oxides in the $R_2O(K_2O, Na_2O) - CaO - BaO - B_2O_3 - Al_2O_3 - SiO_2$ system was found to be optimal for glass formation (%): 18 – 60 SiO_2, 5 – 16 B_2O_3, 4 – 30 R_2O in the ratio of alkaline oxides (parts by weight): $R_2O = 1.3Na_2O + 1.0K_2O$.

The content of R_2O, B_2O_3, and SiO_2 varied according to the established limits (Fig. 1), and based on this, the optimum composition region (*1 – 3 – 5*) was selected. In order to select the optimum composition of the glass matrix for enamel coatings, the glass formation within the specified region was studied. The variants of model glass mixtures prepared from chemical reagents are given in Table 1.

TABLE 1

Mixture	Mass content, %*				TCLE, $10^{-7} K^{-1}$
	SiO_2	B_2O_3	Na_2O	K_2O	
0	45.6	11.2	13.1	10.1	135
1	48.0	8.0	13.6	10.4	130
2	45.2	10.4	13.8	10.6	125
3	43.0	13.0	13.6	10.4	115
4	44.8	12.8	12.7	9.7	120
5	48.0	13.0	10.7	8.3	115
6	48.0	10.4	12.2	9.4	130
7	46.4	9.6	13.6	10.4	130
8	44.8	12.0	13.1	10.1	117
9	46.4	12.0	12.2	9.4	115

* The content of Al_2O_3, CaO, and BaO was constant and amounted to 7.0, 5.0, and 8.0%, respectively.

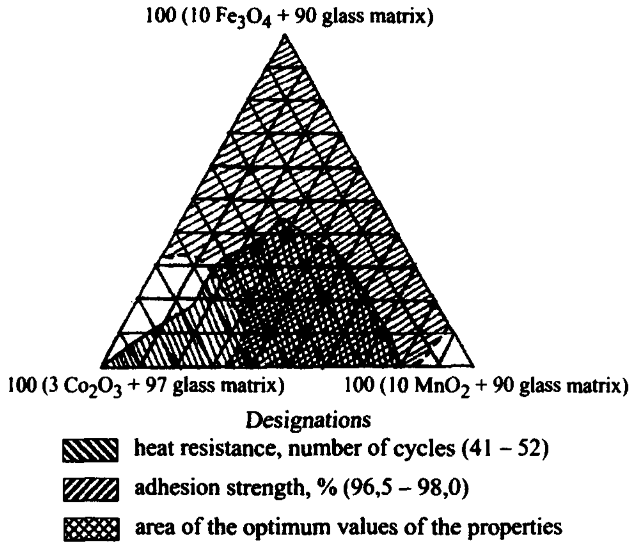

Fig. 2. Diagram of the optimum values of properties.

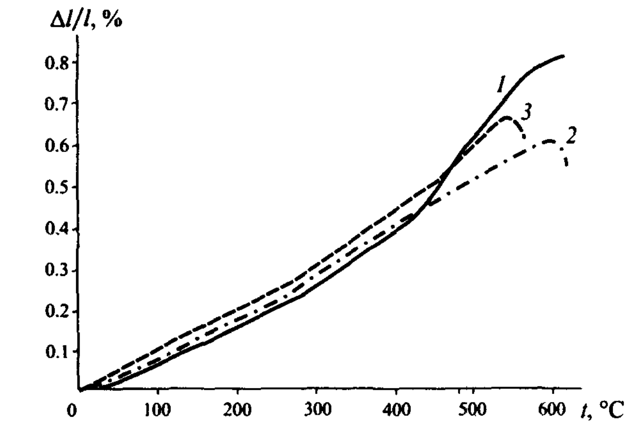

Fig. 3. Temperature dependence of relative elongation of enamels: *1*) copper, *2*) mixture 0; *3*) mixture 0 with additives of 0.99% Co_2O_3, 3.33% Fe_2O_3, and 3.33% MnO_2.

Glasses were melted in an electric furnace at a temperature of 1250°C in an oxidizing medium with rapid cooling in air. The best glass-forming capacity was exhibited by mixtures containing (%): 43 – 48 SiO_2, 8 – 13 B_2O_3, 19 – 24 R_2O. These glasses were selected for further investigation.

The agreement of the coefficients of thermal linear expansion (TCLE) of metal ($162 \times 10^{-7}\ K^{-1}$) and glass has a special significance. The TCLE for the analyzed glasses was $(115 - 135) \times 10^{-7}\ K^{-1}$. It follows from the data in Table 1 that mixture O has a TCLE that is the nearest to the TCLE of copper, and this composition was chosen for further studies.

On firing of the obtained glass matrix, a clear transparent coating appeared on copper, which had a smooth even surface without extraneous inclusions. The optimum firing temperature for the enamel is 850°C. The mean adhesion index measured by the gradual extraction method [2] was 91%, and the heat resistance (the thermal cycling method) was 10 cycles (20 – 400°C). In order to increase the heat resistance and the adhesion strength, Fe_3O_4, MnO_2, and Co_2O_3 additives were introduced in milling of the slip. In order to optimize the process, the experiment was designed using the Sheffe simplex-lattice plan of incomplete third order [3]. The strength of adhesion and the heat resistance were used as response functions. Based on the obtained equations, curves of the optimum values of the properties were constructed (Fig. 2). The adhesion strength of the coatings varied from 92 to 98%, and the heat resistance was 10 – 52 cycles (20 – 400°C).

It was found that the enamels located in the region specified in Fig. 2 and made with the following additives had the optimum qualities (%): 0.51 – 1.98 Co_2O_3, 0 – 4.5 Fe_3O_4, 3.3 – 9.3 MnO_2. On introduction of these additives to enamel slip, the maximum values of adhesion strength constituted 98% and 52 cycles.

The effect of the adhesive additives on the dilatometric parameters of the obtained enamels was studied as well. It was found that on introduction of the specified additives, the TCLE increases from 135×10^{-7} to $160 \times 10^{-7}\ K^{-1}$ (Fig. 3). Moreover, the initial softening point is lowered, and the firing interval of the coating increases: it becomes 750 – 900°C instead of 850 – 900°C in the initial glass matrix. The expansion of the firing interval, in our opinion, can be explained by a shift in the equilibrium of the reaction

$$Mn^{2+} + 2Fe^{3+} = Mn^{4+} + 2Fe^{2+}$$

toward the formation of Mn^{2+} and $2Fe^{3+}$, which weakens to some extent the glass structure [4]. This makes it possible to obtain high-quality enamels on large-scale articles with different thicknesses of component parts.

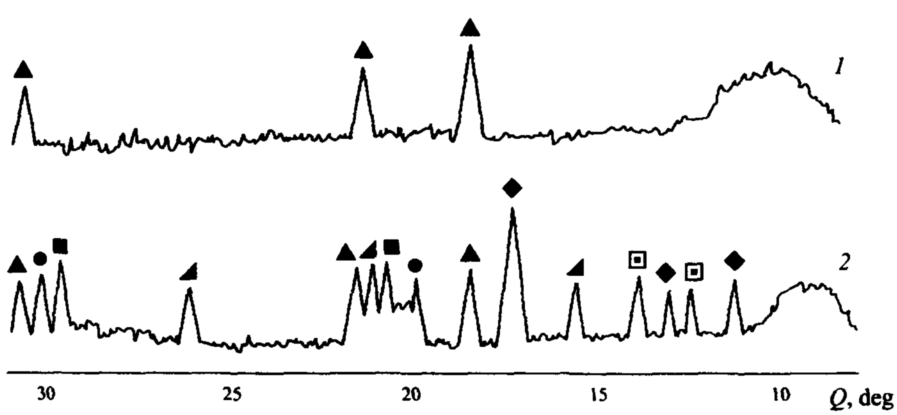

Fig. 4. X-ray patterns of mixture 0 (*1*) and enamels with additives of 0.99% Co_2O_3, 3.33% Fe_2O_3, and 3.33% MnO_2 (*2*). ▲ — Cu_2O; ● — FeO; ■ — $Co_2Fe_9O_{13}$; ◢ — $CuMn_6SiO_{12}$; ◆ — $Cu_2Mn_3O_8$; ▣ — $MnSiO_3$.

In order to determine the factors determining the significant variations in the strength of adhesion of enamel to copper, it was necessary to study the phase composition of the contact layer of the enamel at the boundary of the copper substrate, since it is the phase formation and the phase morphology that determine the variations in the adhesion strength. With this aim, x-ray diffraction analysis of the enamels was carried out on a DRON-15 device. Figure 4 shows the x-ray patterns of the initial glass matrix and the compositions with additives of Fe_3O_4, MnO_2, and Co_2O_3 which have the optimum properties. It was found that in the presence of the specified additives, spinel-type crystalline compounds ($Cu_2Mn_3O_8$) are formed in the coating structure, as well as manganese silicate $MnSiO_3$ and its solid solutions with cupric oxide $CuMn_6SiO_{12}$. The presence of these compounds in the transitional layer can account for a stronger adhesion of this coating to copper and its increased heat resistance.

Thus, the performed experiments make it possible to recommend for industrial use the developed optimum compositions and the technology of preparation of one-coat glass enamel coatings.

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